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MATERIALS ENGINEERING | RESEARCH ARTICLE

Electrochemical analysis of the corrosion inhibition properties of 4-hydroxy-3-methoxybenzaldehyde on low carbon steel in dilute acid media

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Abstract: The electrochemical behaviour of low carbon steel in 1 M H_2SO_4 and HCl acid was studied in the presence of 4-hydroxy-3-methoxybenzaldehyde (HMD) as the inhibiting organic compound through weight loss and potentiodynamic polarization technique. Results show HMD has strong corrosion inhibition effects on the steel in the acid solution. HMD performed excellently at all concentrations studied with optimal inhibition efficiency of 96.6 and 92.5% from weight loss analysis and 88.81 and 91.35% for potentiodynamic polarization tests in H_2SO_4 and HCl. The compound showed mixed inhibition properties in both solutions. Data from statistical analysis through ANOVA shows the overwhelming influence of inhibitor concentration in H_2SO_4 and exposure time in HCl on the inhibition efficiency of the organic compound. Adsorption of the compound obeyed the Langmuir isotherm. Thermodynamic calculations showed strong physiochemical interactions and spontaneous adsorption mechanism.

Subjects: Applied & Industrial Chemistry; Chemistry; Environmental Chemistry; Materials Chemistry; Materials Science; Metals & Alloys; Physical Chemistry

Keywords: adsorption; corrosion; carbon steel; inhibitor; hydrochloric; sulphuric

ABOUT THE AUTHOR

Roland T. Loto is a proven scholar and research scientist in the field of metallic corrosion reactions phenomena, corrosion measurement, control and prevention covering a very broad spectrum of technical areas and activities. He has a significant number of research publications including reviews in top international journals, conference proceedings and has consistently served as reviewer in respectable journals due to his intensive knowledge and technical expertise. He has undertaking a number renowned engineering research in collaboration with research institutes and educational institutions. His in-depth knowledge and experience in research experimentation is basically aimed at proffering solutions to the current depreciating effect of metallic degradation and failure in service in various engineering applications.

PUBLIC INTEREST STATEMENT

The economic impact and problems resulting from corrosion has drawn strong attention from scientists and engineers worldwide. Corrosion of mild steel in industrial environments is a major concern in chemical processing plants, oil and gas industry, manufacturing, automobile industry, marine operations, boiler plants and power generation plants due to the considerable cost involved in the replacement of metallic parts in their various applications. The consequence often leads to plant shutdowns, breakdown of industrial equipment, reduced efficiency, industrial downtime, high maintenance cost due to replacement of damaged part, wastage of valuable resources and expensive overdesign. A great number of studies have being devoted to the subject of corrosion inhibitors. Corrosion inhibition is of great practical importance, being extensively employed in curtailing wastage of engineering materials and minimizing costs of corrosion control.

1. Introduction

Acid solutions are commonly used in chemical industries for production of detergents, synthetic resins, dyestuffs, pharmaceuticals, petroleum catalysts, insecticides and antifreeze etc. as well as in various processes such as paper sizing, water treatment, oil well acidicizing, aluminium reduction and removal of scales from metallic surfaces, most especially carbon steels (Greenwood & Earnshaw, 1997). Carbon steel is a major material of construction, extensively used in chemical and allied industries for handling alkalis, acids and salt solutions due to its easy availability, low cost and uncomplicated fabrication (Melchers & Jeffrey, 2004, 2005; Saha, Kurmaih, & Hakerman, 1955; Singh, Ebenso, & Quraishi, 2012). As a result it corrodes when exposed to various industrial environments and service conditions. The addition of inhibitors protects the metal against corrosion effectively. Inhibitors are one of the most practical methods for protection against corrosion, especially in acidic media (Xianghong & Guannan, 2005). The use of corrosion inhibitors has considerably increased in recent years due to increase in awareness of corrosion worldwide. They play an important role in controlling corrosion of metals (Quraishi & Sardar, 2001). The applicability of organic compounds as corrosion inhibitors for metals in acidic media has been recognized for a long time (Ajmal, Mideen, & Quraishi, 1994; Bethencourt, Botana, Calvino, & Marcos, 1998; El Achouri et al., 2001; El-Etre, 1998; El-Rehim, Ibrahim, & Khaled, 1999; El-Sayed, 1997). Existing data show that most organic inhibitors act by adsorption on the metal surface. Phthalocyanine blue dye was evaluated for its corrosion inhibition and adsorption properties on carbon steel in dilute sulfuric acid through potentiodynamic polarization, electrochemical impedance spectroscopy and weight loss analysis at very low concentration. Results showed that it is an excellent inhibitor with anodic type inhibition and strong passivation characteristics (Valle-Quitana, Dominguez-Patiño, & Gonzalez-Rodriguez, 2014). Ochoa, Moran, and Pébère (2004) studied the synergistic effect of phosphonocarboxylic acid salts and fatty amines on carbon steel in NaCl solution through electrochemical impedance measurements and X-ray photoelectron spectroscopy. Result showed that the combined admixture effectively inhibited the corrosion of the steel through adsorption. Oguzie, Unaegbu, Ogukwe, Okolue, and Onuchukwu (2004) concluded from gravimetric analysis that indigo dye adsorbed onto mild steel according to Frumkins and Flory–Huggins isotherm model in dilute sulphuric acid through chemisorption mechanism inhibiting its corrosion. His work on the inhibitive effect of congo red dye on the mild steel corrosion in sulphuric acid solution showed that the compound adsorbed onto the steel through physiochemical mechanism in accordance with Flory–Huggins isotherm model only (Oguzie, 2004). Rosliza, Nora'aini and Wan Nik (2010) studied the effect of vanillin on the corrosion inhibition of aluminum alloy in marine environment. The parameters from the electrochemical techniques applied confirmed excellent inhibition properties. Adsorption of the compound was found to obey the Langmuir adsorption isotherm. The effect of vanillin on the corrosion behavior of AA6061 Al alloy in NaCl solution was studied by Shahidi, Mansouri, Bahrami, and Hosseini (2015) through electrochemical techniques. Results showed that the organic compound adsorbed strongly onto the steel at very low concentrations with mixed type inhibition efficiency characteristics. Apricot juice showed good corrosion inhibition and physisorption adsorption properties on mild steel in dilute H_3PO_4 acid solution from the work of Aprael, Anees, and Rafal (2013) through weight loss analysis and statistical studies. The electrochemical behaviour of mild steel in HCl and H_2SO_4 acid media in the presence of N-(2-thiophenyl)-N/-phenyl thiourea showed the compound to be an efficient anodic inhibitor with greated inhibition efficiency in HCl than in H_2SO_4 media. Adsorption was observed to obey Temkins' adsorption isotherm (Shetty, Shetty, & Nayak, 2006). The adsorption occurs through heteroatoms such as nitrogen, oxygen, phosphorus and sulphur, triple bonds or aromatic rings. These compounds adsorbed on the metallic surface blocking the active corrosion sites. The adsorption behavior of organic molecules on the surface of metals depends on the molecular structure of the compounds, surface charge density and zero charge potential of metals (Ai, Guo, Qu, Chen, & Zheng, 2006). 4-hydroxy-3-methoxybenzaldehyde has been previously studied for its corrosion inhibiting properties on aluminium in HCl and seawater however literature on its inhibiting properties on mild steel is rare (El-Etre, 2001; Rosliza et al., 2010). This research aims to investigate the inhibiting influence of 4-hydroxy-3-methoxybenzaldehyde on low carbon steel corrosion in 1 M H_2SO_4 and HCl acid solution through weight loss analysis, potentiodynamic polarization test and optical microscopy.

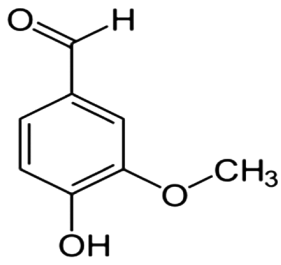


Figure 1. Chemical structure of 4-hydroxy-3-methoxybenzaldehyde (HMD).

2. Experimental procedure

2.1. Material

The low carbon steel utilized for this research was sourced from the open market and analyzed at the Advanced Materials and Tribo-corrosion Research Laboratory, Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, Pretoria, South Africa. The steel has the percentage nominal composition of 0.401C, 0.169Si, 0.440Mn, 0.005P, 0.012S, 0.080Cu, 0.008Ni, 0.025Al and 98.86Fe.

2.2. Inhibitor

4-hydroxy-3-methoxybenzaldehyde (HMD) solid white powdery granules obtained from Merck KGaA, EMD Millipore Corporation, Billerica, USA was the inhibiting compound employed. The structural formula of HMD is shown in Figure 1. The molecular formula is $C_8H_8O_3$, while the molar mass is 152.15 g mol^{-1}.

HMD was prepared and studied in molar concentrations of 0.008, 0.016, 0.025, 0.033, 0.041 and 0.049 respectively.

2.3. Test media

1 M of H_2SO_4 and 1 M HCl acid solution of 200 ml each prepared from deionized water with 1.5% recrystallized sodium chloride of analar grade were used as the corrosion test media.

2.4. Preparation of test specimens

The low carbon steel rods with cylindrical diameter of 14 mm were mechanical cut into specific number of test samples with average dimensions in length of 10 mm. A 3 mm hole was drilled at the steel center for suspension and observation during the experimentation. The steel samples were thereafter carefully cleansed with deionized water and dried with acetone in preparation for weight loss analysis. Metallographic preparation for potentiodynamic polarization tests involved mounting of the steel samples in resin and grinding of their exposed surface with silicon carbide abrasive papers of 80, 120, 220, 800 and 1,000 grits before polishing with 6–1 µm diamond paste. The samples were thereafter rinsed with distilled water and dried with acetone.

2.5. Weight-loss measurement

Weighted steel samples were individually immersed in 200 ml of the acid media at predetermined concentrations of the HMD for 504 h at ambient temperature. The steel samples were weighed every 72 h after been washed with deionized water and dried with acetone for accurate readings. Graphical illustrations of corrosion rate (mm/y) (calculated) vs. exposure time (h) (Figures 2(a) and 3(a)) for the two acid media and those of percentage inhibition efficiency (*IE*) (calculated) vs. exposure time (h) (Figures 2(b) and 3(b)) were made from tabulated results (Tables 1 and 2).

The corrosion rate (*R*) was calculated from Equation (1):

$$R = \left[\frac{87.6W}{DAT}\right] \quad (1)$$

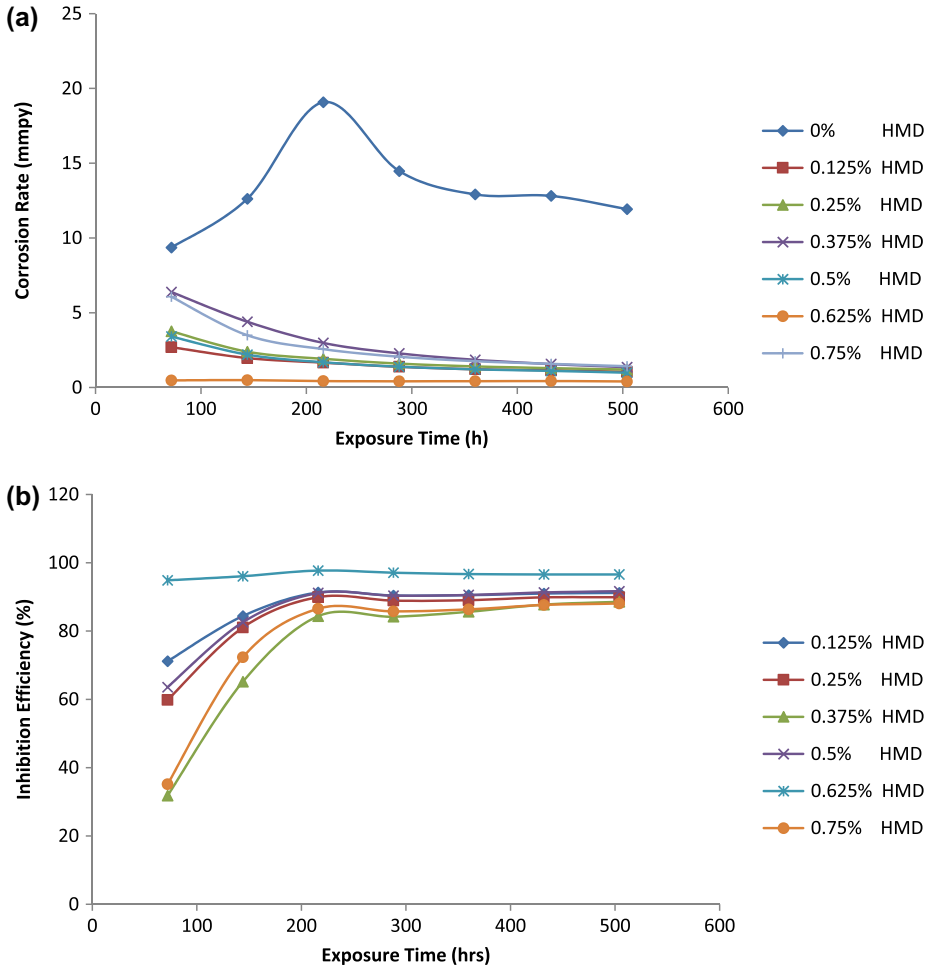


Figure 2. Graph of (a) corrosion rate vs. exposure time (b) inhibition efficiency vs. exposure time in 1 M H_2SO_4 at 0–0.049 M HMD.

where W is the weight loss in milligrams, D is the density in g/cm^2, A is the area in cm^2, and T is the time of exposure in hours. The IE was determined from Equation (2):

$$IE = \left[\frac{R_1 - R_2}{R_1}\right] \times 100 \tag{2}$$

R_1 and R_2 are the corrosion rates with and without predetermined concentrations of HMD. The IE was determined every 72 h through the study. The surface coverage is determined from Equation (3):

$$\theta = \left[1 - \frac{W_2}{W_1}\right] \tag{3}$$

where θ is the substance amount of adsorbate adsorbed per gram (or kg) of the adsorbent. W_1 and W_2 are the weight loss of the low carbon steel in the inhibited and uninhibited acid solutions.

2.6. Potentiodynamic polarization analysis

Potentiodynamic polarization analyses were performed using cylindrical steel samples embedded in resin mounts with exposed surface of 154 mm^2. The analyses were performed at ambient temperature of 25°C with Digi-Ivy potentiostat. A platinum rod was used as the counter electrode and silver chloride electrode (Ag/AgCl) with pH of 6.5 was used as the reference electrode. The potentials were cursorily examined from −1.5 V to +1.5 V vs. OCP at a scan rate of 0.002 V/s. The corrosion current

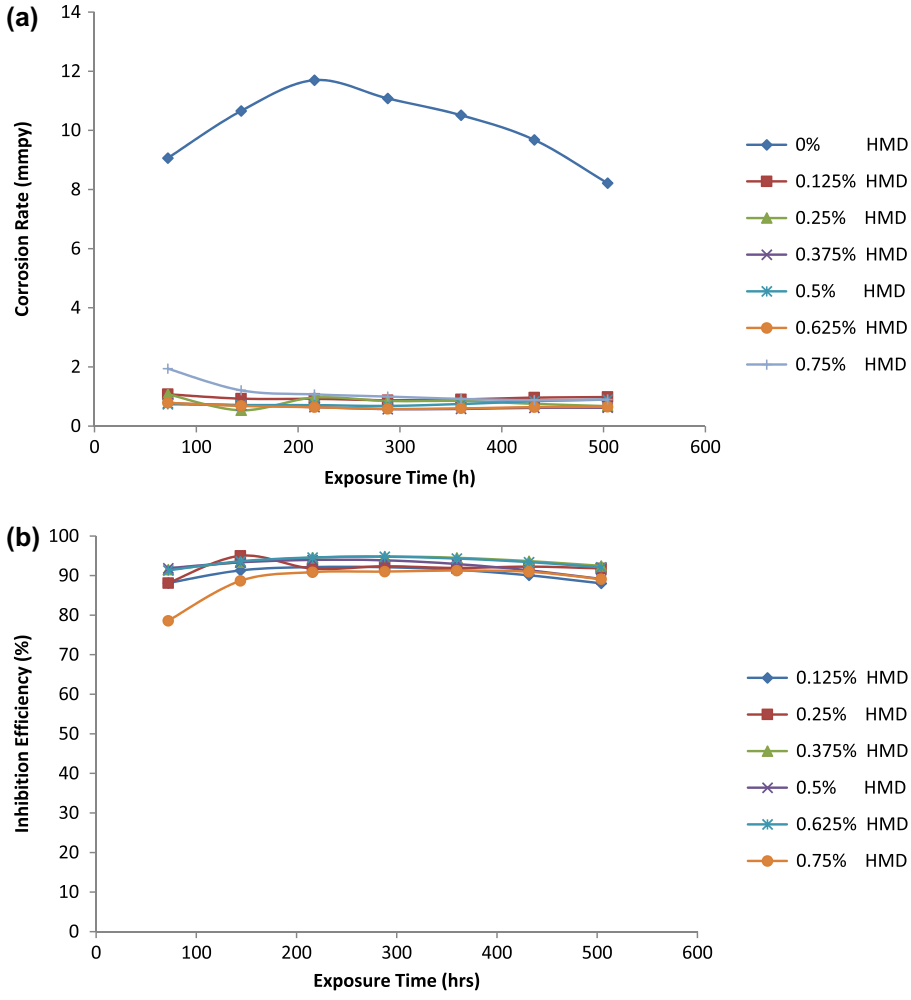


Figure 3. Graph of (a) corrosion rate vs. exposure time (b) inhibition efficiency vs. exposure time in 1 M HCl at 0–0.049 M HMD.

Table 1. Data obtained from weight loss measurements for low carbon steel in 1 M H_2SO_4 at specific concentrations of HMD after 504 h

Sample	Corrosion rate (mm/y)	Surface coverage (θ)	Weight loss (mg)	Inhibition efficiency (%)	Inhibitor concentration (%)	Inhibitor concentration (M)
A	11.9	0	4.036	0	0	0
B	1.0	0.912	0.355	91.2	0.0125	0.008
C	1.2	0.899	0.407	89.9	0.025	0.016
D	1.4	0.886	0.461	88.6	0.0375	0.025
E	1.0	0.917	0.336	91.7	0.05	0.033
F	0.4	0.966	0.137	96.6	0.0625	0.041
G	1.4	0.881	0.481	88.1	0.075	0.049

(i_{corr}), corrosion current density (I_{corr}) and corrosion potential (E_{corr}) were determined from the Tafel plots of potential vs. log I_{corr}. The corrosion rate (R) was calculated from Equation (4):

$$R = \frac{0.00327 \times i_{corr} \times E_q}{D} \quad (4)$$

Table 2. Data obtained from weight loss measurements for low carbon steel in 1 M HCl at specific concentrations of HMD after 504 h

Sample	Corrosion rate (mm/y)	Surface coverage (θ)	Weight loss (mg)	Inhibition efficiency (%)	Inhibitor concentration (%)	Inhibitor concentration (M)
A	8.21	0	2.778	0	0	0
B	0.98	0.880	0.332	88.0	0.0125	0.008
C	0.67	0.918	0.227	91.8	0.025	0.016
D	0.62	0.925	0.210	92.5	0.0375	0.025
E	0.89	0.891	0.302	89.1	0.05	0.033
F	0.65	0.921	0.219	92.1	0.0625	0.041
G	0.90	0.891	0.303	89.1	0.075	0.049

where i_{corr} is the current density in A/cm^2, D is the density in g/cm^3, E_q is the specimen equivalent weight in grams. The percentage inhibition efficiency (IE) was determined from Equation (5):

$$IE = 1 - \left[\frac{R_2}{R_1}\right] \times 100 \tag{5}$$

$R_1$and R_2 are the corrosion current densities in absence and presence of HMD respectively.

2.7. Optical microscopy characterization

The surface morphology and topography of the inhibited and uninhibited steel samples were investigated after weight-loss analysis in 1 M H_2SO4 and 1 M HCl solutions using OMAX Trinocular metallurgical microscope for which optical micrograph were obtained.

2.8. Statistical analysis

Two-factor single level statistical analysis with ANOVA (*F*-test) was applied to evaluate the statistical importance of HMD concentrations and time of exposure on inhibition efficiency values of HMD in H_2SO_4 and HCl acid solutions. The *F*-test was used to study the quantitative value of variation within each of the samples relative to the amount of variation between the samples.

The sum of squares among columns (exposure time) was obtained with Equation (6):

$$SS_c = \frac{\sum T_c^2}{nr} - \frac{T^2}{N} \tag{6}$$

Sum of squares among rows (HMD concentration) was obtained with Equation (7):

$$SS_r = \frac{\sum T_r^2}{nc} - \frac{T^2}{N} \tag{7}$$

While the total sum of squares was obtained from Equation (8).

$$SS_{Total} = \sum x^2 - \frac{T^2}{N} \tag{8}$$

3. Results and discussion

3.1. Weight-loss measurements

Weight-loss of the low carbon steel during the exposure period with and without specific concentrations of HMD in 1 M H_2SO_4 and HCl test solutions at ambient temperature was studied. The data for weight-loss (*W*), corrosion rate (*R*) and percentage inhibition efficiency (*IE*) in both acids are shown in Tables 1 and 2. Figures 2(a), (b) and 3(a), (b) shows the graphical plot of corrosion rate and percentage inhibition efficiency vs. exposure time in H_2SO_4 and HCl acid solutions respectively. The remarkable difference between the inhibited and uninhibited low carbon steel samples in the acid solutions as shown the figures earlier mentioned due to the presence of HMD and its electrochemical influence on the oxygen reduction, hydrogen evolution and oxidation corrosion processes which results in the effective protection of the exposed steel surface. In Figure 2(a) there is a progressive decrease in corrosion rate at the early onset of the exposure hours from 0.008 to 0.0033 M HMD and 0.049 M HMD concentration till 288 h exposure, after which the corrosion rate remains fairly constant, till the end of the exposure period. Figure 3(a) shows a slightly different phenomenon in HCl acid compared to H_2SO_4 where the corrosion rates were instantaneously very low in value due to the strong electrochemical action of HMD. This suggests that HMD inhibits corrosion more rapidly in HCl compared to H_2SO_4 acid, but the resultant effects are generally the same. The same phenomenon is observed in Figures 2(b) and 3(b) where there was a gradual increase in the inhibition efficiency of HMD in Figure 2(b) before remaining generally constant as compared to Figure 3(b).

HMD being an organic compound, its inhibition mode is through adsorption to the steel surface, due to its influence on the electrochemical reactions mechanism within the acid test solutions (Hackerman, Snavely, & Payne, 1966) as shown in the surface coverage values in Tables 1 and 2. The HMD molecules adhere themselves onto the steel surface through adsorption inhibiting the electrolytic transport and diffusion of the corrosive species responsible for the deterioration of the steel. Visual observation of the steel samples in the test solutions suggests that cathodic inhibition plays a significant role in the inhibition characteristics of HMD. Cathodic inhibitors act by either slowing the cathodic reaction itself or selectively precipitating on cathodic areas to limit the diffusion of reducing species to the surface (Agarwal & Landolt, 1998; Corrosion Inhibitors, n.d.). Organic inhibitors are known to generally have heteroatoms such as O, N, and S which have higher basicity and electron density and thus act as corrosion inhibitor. These heteroatoms are the vital sites for the adsorption mechanism on the steel surface (Felicia, Santhanalakshmi, Wilson, John, & Susai, 2004). The inhibition efficiency of HMD as shown in the figures mentioned above is generally not proportional to its concentration and corrosion rate, but quantitatively commensurate to the amount of adsorbed HMD on the steel surface. Corrosion reactions are prevented from occurring over the active sites of the metal surface influenced by HMD molecules. Comparison of the uninhibited low carbon steels (0 M HMD) in H_2SO_4 and HCl solution with the inhibited solutions (0.008–0.049 M HMD) in Tables 1 and 2 evidently confirms that HMD at all concentrations effectively reduced the corrosion rates of the steel, thus protecting it.

3.2. Polarization studies

The influence HMD inhibitor concentration on the polarization diagrams of the low carbon steel in 1 M H_2SO_4 and HCl solutions was studied. Figure 4 shows the polarization plots of the relationship of the log of current density *I* (Acm^{-2}) vs. the applied potential *E* (V) on the low carbon steel for HMD in 1 M H_2SO_4, while Figure 5 illustrates the plot of *IE* vs. HMD inhibitor concentration for potentiodynamic polarization test in the acid. Tables 3 and 4 show the potentiodynamic data obtained from the acid test solutions. As shown in Table 3 the inhibition efficiency of HMD is independent of its concentration value in the test solution. Increase in HMD concentration does not result in any change in inhibition efficiency. The inhibition efficiency data in Table 3 are generally similar form the lowest to the highest HMD concentration (0.008–0.049 M), an indication of HMD potency to counteract the corrosive effect of the acid test solution at all concentrations. The data for the parameters on the table shows that HMD inhibited the electrochemical process responsible for corrosion.

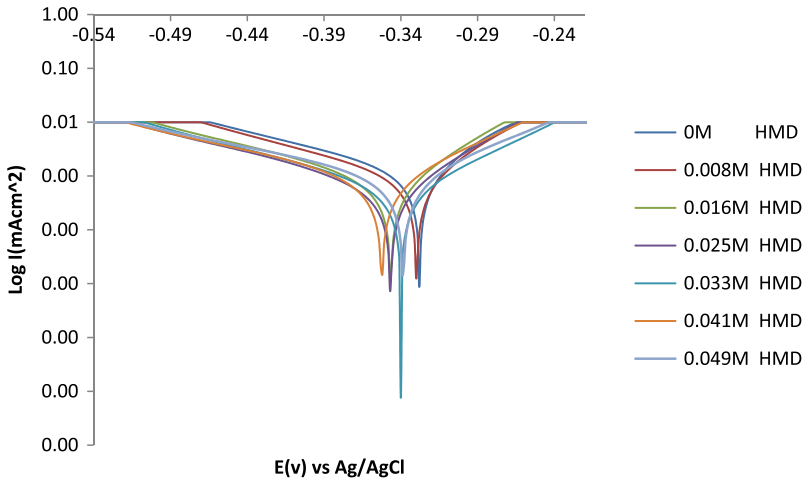


Figure 4. Potentiodynamic polarization plot for the low carbon steel in 1 M H_2SO_4 acid at specific HMD concentrations (0.008–0.049 M).

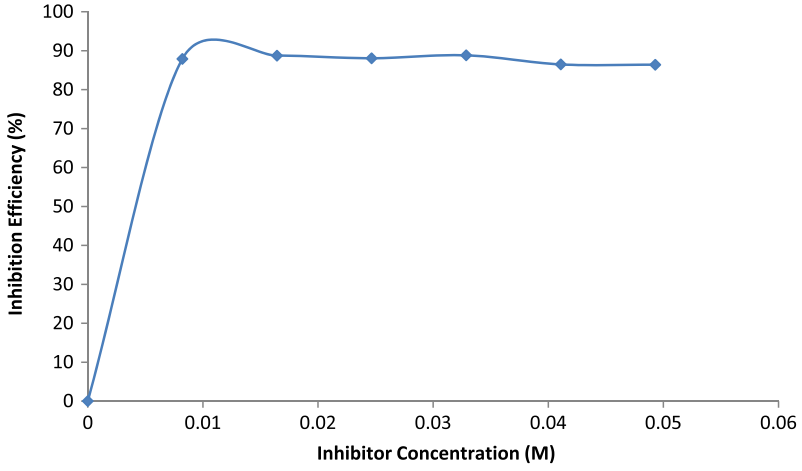


Figure 5. Plot of *IE* vs. HMD inhibitor concentration for potentiodynamic polarization test in 1 M H_2SO_4.

Table 3. Potentiodynamic polarization test data for the low carbon steel in 1 M H_2SO_4 at specific HMD concentrations

Sample	Inhibitor conc. (M)	Corr. rate (mm/y)	Inhibition efficiency (%)	Corr. current (A)	Corr. current density (A/cm²)	Corr. potential (V)	Polarization resistance, R_p (Ω)	B_c	B_a
A	0	11.98	0	1.59E-03	1.03E-03	−0.328	3.90	−0.715	0.014
B	0.008	1.45	87.90	1.93E-04	1.25E-04	−0.330	21.10	−0.767	0.057
C	0.016	1.35	88.73	1.79E-04	1.16E-04	−0.347	57.80	−0.747	0.111
D	0.025	1.43	88.06	1.89E-04	1.23E-04	−0.347	46.00	−0.773	0.070
E	0.033	1.34	88.81	1.77E-04	1.15E-04	−0.340	50.50	−0.763	0.075
F	0.041	1.62	86.48	2.14E-04	1.39E-04	−0.352	73.60	−0.683	0.127
G	0.049	1.63	86.39	2.16E-04	1.40E-04	−0.339	60.60	−0.637	0.113

Table 4. Potentiodynamic polarization test data for the low carbon steel in 1 M HCl at specific HMD concentrations

Sample	Inhibitor conc. (M)	Corr. rate (mm/y)	Inhibition efficiency (%)	Corr. current (A)	Corr. current density (A/cm^2)	Corr. potential (V)	Polarization resistance, R_p (Ω)	B_c (V/dec)	B_a (V/dec)
A	0	7.98	0	1.06E-03	6.86E-04	−0.306	8.00	−0.798	0.028
B	0.008	0.88	88.97	1.17E-04	7.60E-05	−0.309	46.40	−0.810	0.116
C	0.016	0.97	87.84	1.28E-04	8.30E-05	−0.284	96.60	−0.618	0.161
D	0.025	0.70	91.23	9.24E-05	6.00E-05	−0.344	81.80	−0.800	0.117
E	0.033	0.69	91.35	9.09E-05	5.90E-05	−0.347	88.30	−0.798	0.123
F	0.041	0.92	88.47	1.22E-04	7.90E-05	−0.341	76.00	−0.762	0.133
G	0.049	0.93	88.35	1.23E-04	8.00E-05	−0.336	70.50	−0.760	0.132

Figure 6 shows the polarization plots of the relationship of the log of current density I (Acm^2) vs. the applied potential *E* (mV) on the low carbon steel for HMD in 1 M HCl, while Figure 7 shows the plot of *IE* vs. HMD inhibitor concentration for potentiodynamic polarization test in the acid. The potentiodynamic data obtained in HCl solution are shown in Table 4 where the inhibition efficiency are generally similar at all concentrations of HMD with slight increase at 0.025–0.033 M HMD concentration. The corrosion rate values in HCl are significantly lesser than in H_2SO_4 due to the more aggressive nature of SO_4^{2-} ions in H_2SO_4 solution. HMD exhibited similar potency in HCl as in H_2SO_4 in inhibiting corrosion of the carbon steel samples under study.

Comparative observation of the polarization plot in Figure 4 and the corrosion potential in Table 3 shows that the corrosion potential shifts towards more negative potentials with increase in HMD concentration. The addition of HMD causes a remarkable decrease in the corrosion rate, i.e. shifts both the anodic and cathodic curves to lower current densities. This may be ascribed to adsorption of inhibitor over the corroded surface (Mu, Li, Qu, & Zhou, 2006). This phenomenon is attributed to anodic inhibition. Anodic inhibition involves surface coverage through film formation as a result of the interaction of HMD molecules with the steel surface. This does not negate cathodic inhibition which involves increase in surface impedance and inhibition of hydrogen evolution and oxygen reduction reactions. The major shift in corrosion potential is 24 mV indicating mixed type inhibition in H_2SO_4 acid. The polarization plot in Figure 6 and the corrosion potential in Table 4 shows that the shift in corrosion potential in both directions i.e. 22 mV in the positive direction and 41 mV in the negative direction. The values show that HMD inhibition in HCl is characteristically mixed type but to a slight degree cathodic (Şahin, Bilgiç, & Yılmaz, 2002). Thus in HCl steel passivation through adsorption is as a result of the deposition of HMD cations on the surface due to interaction between the inhibitor and the oxidized metal surface which effectively seals the surface against further reaction; however the cathodic process predominates over the anodic.

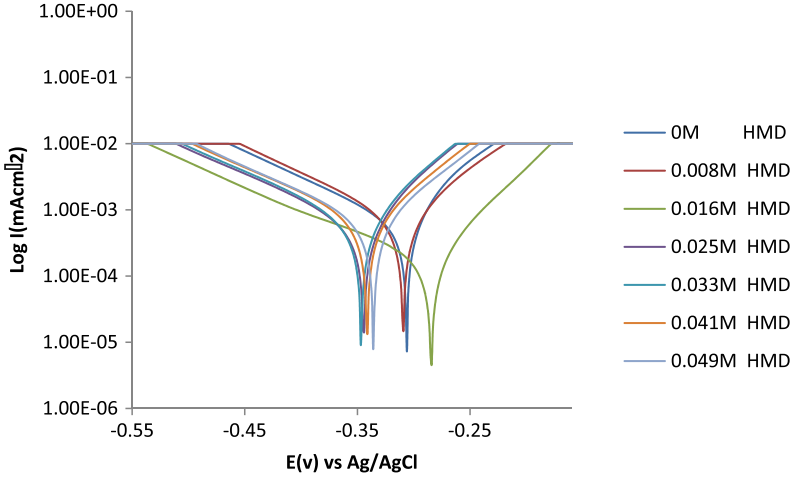


Figure 6. Potentiodynamic polarization plot for the low carbon steel in 1 M HCl acid at specific HMD concentrations (0.008–0.049 M).

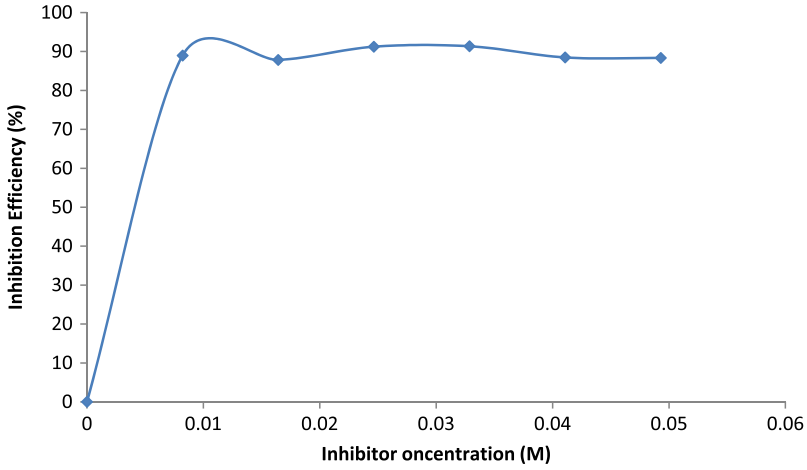


Figure 7. Plot of *IE* vs. HMD inhibitor concentration for potentiodynamic polarization test in 1 M HCl.

The corrosion inhibition behaviour of HMD in HCl and H_2SO_4 acid media with respect to concentration contrasts the results obtained from the work of Rosliza et al. (2010) and El-Etre (2001) where the same organic compound was used on aluminium in seawater and HCl acid media. The inhibition efficiency of the compound was observed to increase with increase in concentration (Inhibitor Efficiency, n.d.). The synergistic effect of HMD with protocatechualdehyde was studied by Emregül and Hayvalı (2004). Result show that the inhibition efficiency of the combined admixture increased with increase in concentration. These observations were confirmed from the results obtained from the use of non-ionic surfactants obtained from HMD in the combined mixture of saltwater and bentonite clay by Negm et al. (2015), however the compounds mentioned by the different authors displayed similar inhibition type (mixed type inhibition) with HMD and obeyed the Langmuir adsorption isotherm.

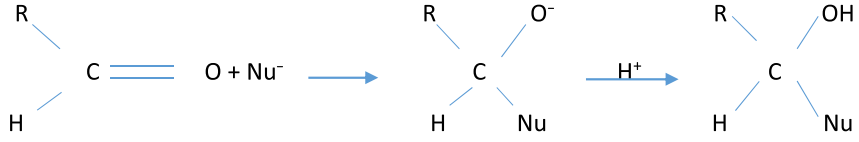
The I_{corr} in Tables 3 and 4 associated with corrosion significantly decreased with increase in HMD concentration. In the presence of HMD, the insignificant change of B_c in both acid solutions and the observable change of B_a between the inhibited and uninhibited steel samples confirms that the corrosion mechanism of the cathodic process remains unchanged while the anodic dissolution of the steel was arrested, hence the difference in value of the anodic current. The results suggest that HMD acts by simple blocking of the available surface area [32], i.e. HMD decreases the surface area for corrosion through anodic inhibition. Furthermore, the inhibition efficiencies obtained from weight loss and polarization curves are in reasonably good agreement.

3.3. Inhibition mechanism

The inhibition performance of HMD is proportional to the extent to which it adsorbs over the metal surface. Adsorption depends on the molecular structure of the inhibitor, the surface charge of the metal, and on the type of corrosive media. Mixed type inhibitors have been known to protect metals in three possible ways: electrostatic adsorption, chemisorption and film formation. Electrostatic adsorption is the result of attraction between HMD and the metal surface. The metal surface is positively charged due to ionization (protonation) in the acid solutions which leads to electrostatic attraction of excess Cl^- and SO_4^{2-} anions in the acid media. This causes net negative charge on the metal surface resulting in the adsorption of protonated HMD ions and hence reducing the dissolution of Fe to Fe^{2+} (Martinez, 2002; Unuabonah, Olu-Owolabi, Adebowale, & Ofomaja, 2007). The data on inhibition efficiency and surface coverage in Tables 3 and 4 suggest chemisorption mechanism due to chemical interactions which is responsible for HMD adhesion to the low carbon steel this is confirmed from thermodynamic calculations which will be discussed later. The physicochemical property of HMD is related to its functional groups (aldehyde, hydroxyl, and ether) and their chemical reactivity. Ethers are slightly polar i.e. they have a dipole moment. The C-O-C bond angle within their functional group is about 110°, and the C-O dipoles do not cancel out. However, the presence of two lone pairs of electrons on the oxygen atoms makes hydrogen bonding with water molecules possible

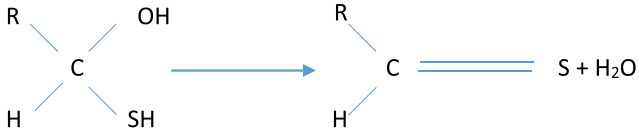
(James, n.d). Ethers are hydrolysed to alcohols in the presence of dilute acid thus increasing their solubility in the test solution. The hydroxyl functional group contains one oxygen atom connected by a covalent bonding to one hydrogen atom. It is the functional group of alcohols. This group has two reactive covalent bonds, the C–O bond and the O–H bond. The electronegativity of oxygen is substantially greater than that of carbon and hydrogen. Consequently, the covalent bonds of this functional group are polarized so that oxygen is electron rich and both carbon and hydrogen are electrophilic (Alcohol Nomenclature, n.d.).

The aldehyde functional group belongs to a class of organic compounds, in which the carbon atom shares a double bond with an oxygen atom, a single bond with a hydrogen atom, and a single bond with other atoms or group of atoms. The double bond between carbon and oxygen is known as the carbonyl group. The reactivity of these compounds arises largely through the polarity of the carbonyl group and the acidity of any α-hydrogen that are present in their structure (Aldehyde Chemical Compound, n.d.). Aldehydes are polar molecules, thus they react with the nucleophide atoms of the corrosive species (Cl^- and SO_4^{2-}) with a deficiency of electrons to form a new covalent bond. The reaction of carbonyl group begins with an attack of a nucleophile (abbreviated as Nu^-) at the carbon atom of a carbonyl group, followed by combination of the now-negatively charged oxygen with a positive hydrogen ion.



(9)

Under the acidic conditions the positive hydrogen ion adds to the carbonyl oxygen first and then the nucleophile attacks the carbonyl carbon resulting in the loss of water. The newly formed –OH group leaves together with hydrogen from an adjoining atom. The result is formation of a double bond between the carbon and the nucleophile giving a C=S bond.



(10)

The interaction of the pi-orbitals of HMD functional groups with d-orbitals of the valence atoms of the metal is responsible for the adsorption bond strength and the nature of the protective film.

3.4. Adsorption isotherm

Further analysis of the corrosion inhibition mechanism of HMD obtained from its adsorption characteristics and behaviour on the metal surface. Effective corrosion inhibition due to the nature of the chemical bond between HMD molecules and the valence metal ions must be stronger than the interaction between HMD and water molecules. The adsorption of HMD at the metal/solution interface is due to the formation of electrostatic or covalent bonding between it and the ionized molecules of the metal surface atoms. Langmuir isotherms amongst others best explain the data obtained for HMD adsorption in 1 M H_2SO_4 and HCl solutions.

Adsorption isotherms are of the general form shown in Equation (11).

$$f(\theta, x)\exp(-2a\theta) = KC \tag{11}$$

where $f(\theta, x)$ is the configurational factor subject to the physical model and assumption responsible for the derivation of the isotherm, θ is the surface coverage, C is the inhibitor concentration, "a" is the molecular interaction parameter and K is the equilibrium constant of adsorption process.

The conventional form of the Langmuir isotherm is,

$$\left[\frac{\theta}{1-\theta}\right] = K_{ads}C \tag{12}$$

and rearranging gives

$$\theta = \left[\frac{K_{ads}C}{1+K_{ads}C}\right] \tag{13}$$

where θ is the value of surface coverage on the steel alloy, C is HMD concentration in the acid solution and K_{ads} is the equilibrium constant of the adsorption process. The plots of $\frac{C}{\theta}$ vs. the inhibitor concentration C were linear (Figures 8 and 9) indicating Langmuir adsorption.

The slight divergence of the slopes from unity in Figures 8 and 9 is due to the molecular interaction among the HMD molecules on the metal surface and changes in the values of the Gibbs free energy relative to the surface coverage.

Langmuir isotherm states the following proposition:

(a) The molecular interaction between HMD molecules on the metal surface is constant.

(b) The Gibbs free energy is independent of the value of surface coverage.

(c) The effect of lateral interaction between HMD molecules on the Gibbs free energy is negligible (Feng, Siow, Teo, & Hsieh, 1999).

Langmuir isotherm forecasts agreement between the fitted values but the derived values are less than unity for the slopes thereby indicating slight deviation from the absolute conditions stated in the isotherm.

3.5. Thermodynamics of the corrosion process

The values of Gibbs free energy (ΔG_{ads}) for the adsorption process can be evaluated from the equilibrium constant of adsorption using the equation as shown in Tables 5 and 6.

$$\Delta G_{ads} = -2.303RT \log\left[55.5K_{ads}\right] \tag{14}$$

where 55.5 is the molar concentration of water in the solution, R is the universal gas constant, T is the absolute temperature and K_{ads} is the equilibrium constant of adsorption.

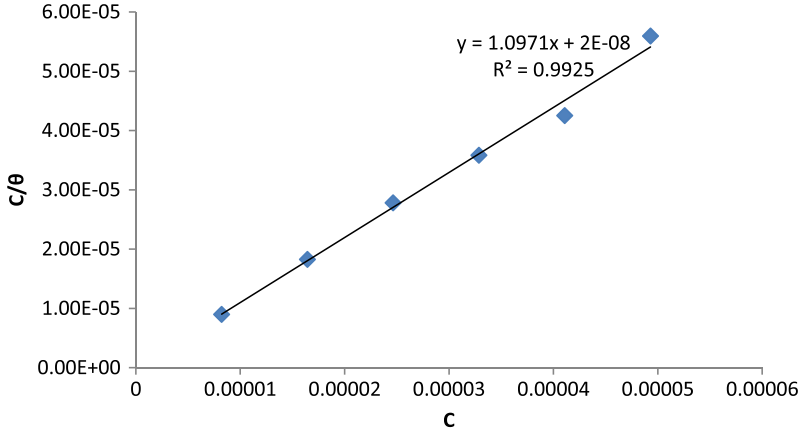


Figure 8. Plot of $\frac{C}{\theta}$ vs. HMD concentration (C) in 1 M H_2SO_4.

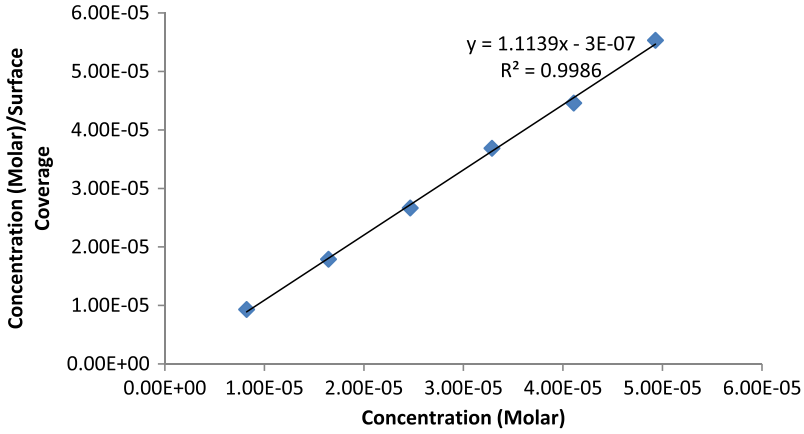


Figure 9. Plot of $\frac{C}{\theta}$ vs. HMD concentration (*C*) in 1 M HCl.

The values of Free energy of Adsorption (ΔG_{ads}) shown in Tables 5 and 6 provides further evidence of minimal divergence from absolute conditions of the Langmuir isotherm model as observed from the differential values of the Free energy of Adsorption (ΔG_{ads}) with respect to the surface coverage (θ) values.

The differential values of ΔG_{ads} in Tables 5 and 6 are due to the non- homogeneous nature of the steel. The topographic sites on the low carbon steel surface are not homogeneous thus the energy of adsorption is not equivalent. The energy of adsorption is subject to the topographic characteristics of metal and flaws (e.g. dislocations, vacancies, voids, inclusion and micro-distortions of crystal lattice) on the metal surface. The negative sign on ΔG_{ads} values depicts the spontaneous nature adsorption of HMD on the metal surface. The calculated values of ΔG_{ads} varies between −34.80 kJ mol^{-1} and −29.52 kJ mol^{-1} in H_2SO_4 solutions while in HCl it varies between −33.95 kJ mol^{-1} and −29.77 kJ mol^{-1}. Values of ΔG_{ads} of about −20 kJ/mol or below relates to weak intermolecular interaction and values of −40 kJ mol^{-1} and above involves electrostatic attractions between the charged molecules and the charged metal i.e. the formation of covalent bond (Hosseini, Mertens, & Arshadi, 2009; Obot, Obi-Egbedi, & Umoren, 2009). The ΔG_{ads} data obtained shows that the adsorption mechanism of HMD on the low carbon steel varies from physiochemical (the combined action of electrostatic attraction and chemical reaction mechanism forming an insoluble protective film on the metal surface) to chemisorption interaction.

3.6. Optical microscopy characterization

The micrographs of the low carbon steel samples before and after the weight loss measurements are shown from Figures 10 to 12. The micrograph of the steel samples before the corrosion test as obtained commercially metallographic preparation of their surfaces at magnifications of ×4, ×10, ×40 and ×100 are presented in Figure 10(a)–(d). Figure 11(a)–(d) shows the micrograph of the steel specimens after the corrosion test without HMD. Its surface morphology significantly contrasts the micrographs in Figure 10. Degradation and surface deterioration of the sample is clearly visible due to corrosion from anions of sulphates and chloride within the acid solution. The anions react with the metal surface through the redox electrochemical process leading to the dissolution of the metal which passes into the solution as Fe^{2+} cations. This observation was noticed during the exposure hours whereby there was a gradual buildup of sediments of iron compounds and significant discoloration of the acid solution. The morphology in Figure 11 shows that the steel is unacceptable for applications in corrosive environments as rapid deterioration occurs. The micrographs of the low carbon steel samples after immersion in the acid solution in the presence of HMD inhibiting compound are shown in Figure 12(a)–(d). In agreement with the results from weight loss and potentiodynamic polarization, the micrograph displays the topography of the steel shielded from corrosion due to the adsorption of HMD compound unto the steel surface.

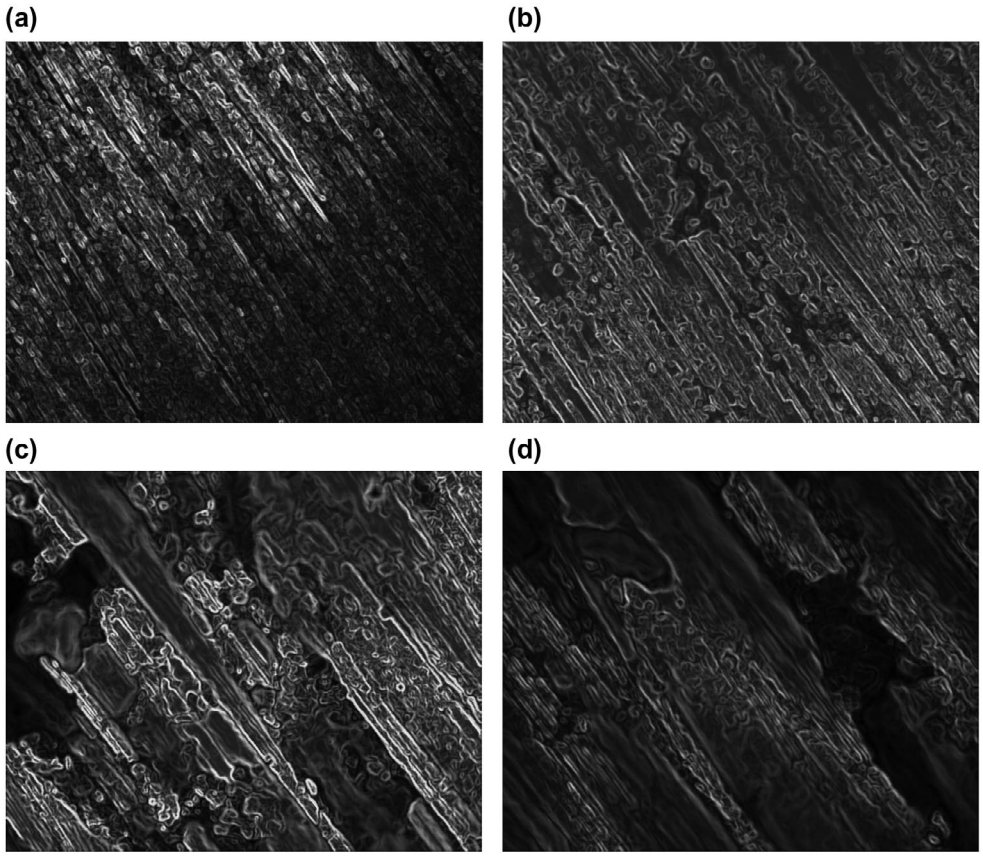


Figure 10. Micrographic images of low carbon steel before exposure to acid solution (a) mag. ×4, (b) mag. ×10, (c) mag. ×100 and (d) mag. ×100.

Table 5. Data obtained for the values of Gibbs free energy, surface coverage and equilibrium constant of adsorption at varying concentrations of HMD in 1 M H_2SO_4

Samples	Surface coverage (θ)	Inhibitor concentration (M)	Equilibrium constant of adsorption (K)	Gibbs free energy (ΔG) (kJ/mol)
A	0	0	0	0
B	0.912	8.22E-06	1,261,462	−34.80
C	0.899	1.64E-05	541,714	−32.70
D	0.886	2.46E-05	315,333	−31.36
E	0.917	3.29E-05	336,197	−31.52
F	0.966	4.11E-05	691,656	−33.31
G	0.881	4.93E-05	150,190	−29.52

Table 6. Data obtained for the values of Gibbs free energy, surface coverage and equilibrium constant of adsorption at varying concentrations of HMD in 1 M HCl

Sample	Surface coverage (θ)	Inhibitor concentration (M)	Equilibrium constant of adsorption (K)	Gibbs free energy (ΔG) (kJ/mol)
A	0	0	0	0
B	0.880	8.22E-06	896,301.8	−33.95
C	0.918	1.64E-05	683,716.9	−33.28
D	0.925	2.46E-05	497,255.6	−32.49
E	0.891	3.29E-05	249,618.7	−30.78
F	0.921	4.11E-05	284,079.9	−31.10
G	0.891	4.93E-05	165,734.7	−29.77

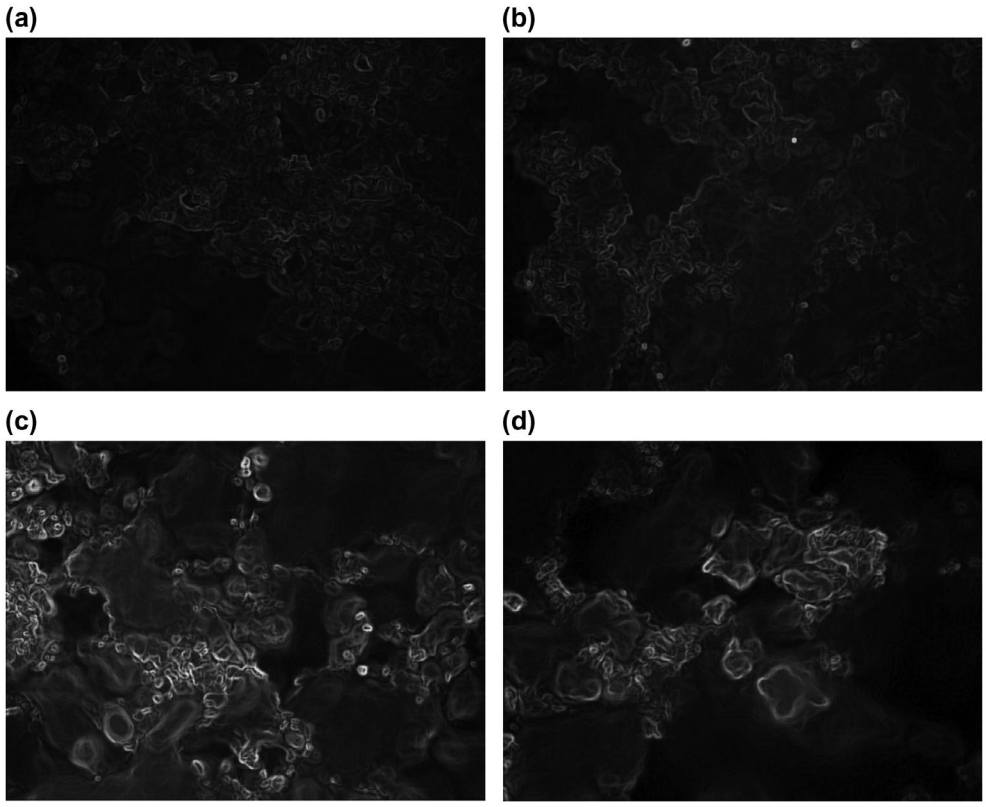


Figure 11. Micrographic images of low carbon steel after exposure to acid solution without HMD compound (a) mag. ×4, (b) mag. ×10, (c) mag. ×40, (d) mag. ×100.

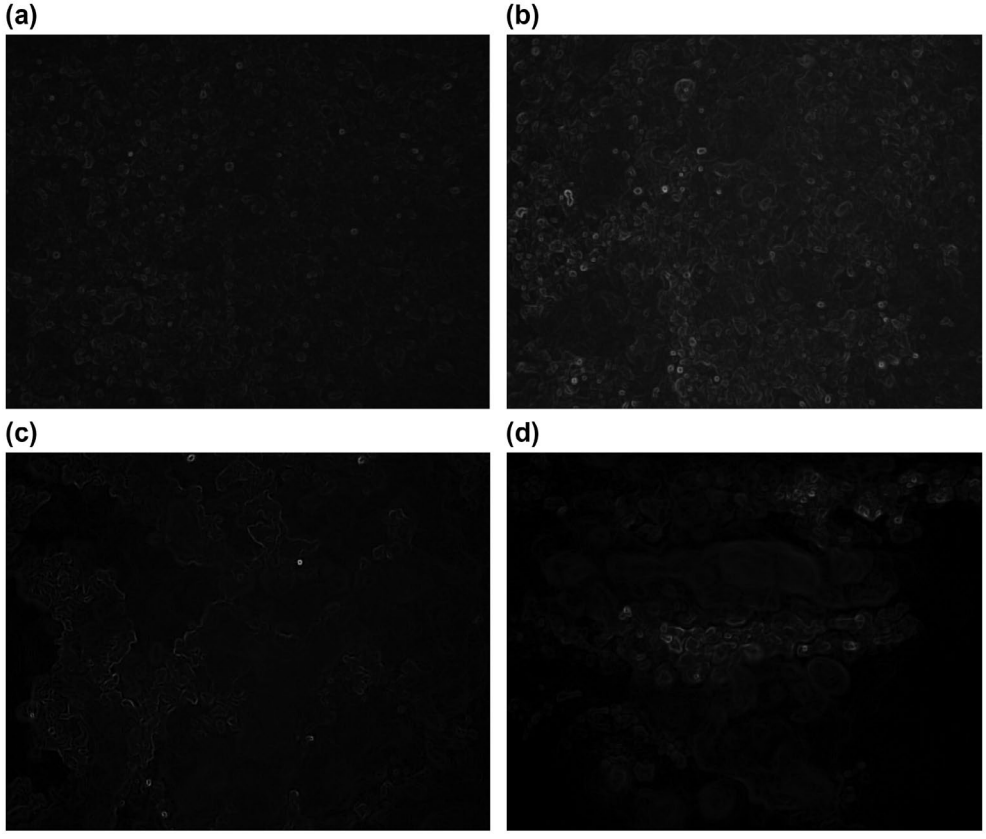


Figure 12. Micrographic images of low carbon steel after exposure to acid solution with HMD compound (a) mag. ×4, (b) mag. ×10, (c) mag. ×40, (d) mag. ×100.

Table 7. Analysis of variance (ANOVA) for inhibition efficiency of HMD inhibitor in 1 M H_2SO_4 (at 95% confidence level)

Source of variation	Sum of squares	Degree of freedom	Mean square	Mean square ratio (*F*)	Min. MSR at 95% confidence level	*F* (%)
					Significance *F*	
Inhibitor concentration	52,215.76	5	10,443.15	18.52	2.53	170.84
Exposure time	−38,567.65	6	−6,427.94	−11.40	2.42	−126.18
Residual	16,916.90	30	563.90			
Total	30,565.02	69				

Table 8. Analysis of variance (ANOVA) for inhibition efficiency of HMD inhibitor in 1 M HCl (at 95% confidence level)

Source of variation	Sum of squares	Degree of freedom	Mean square	Mean square ratio (*F*)	Min. MSR at 95% confidence level	*F* (%)
					Significance *F*	
Inhibitor concentration	59,035.40	5	11,807.08	−11.01	2.53	−250.96
Exposure time	−50,379.03	6	−8,396.51	7.83	2.42	214.16
Residual	−32,180.66	30	−1,072.69			
Total	−23,524.29	69				

3.7. Statistical analysis

Statistical analysis was employed through ANOVA at a confidence level of 95% i.e. a significance level of $\alpha = 0.05$. Data from ANOVA showed that the experimental sources of variation (HMD concentration and time of exposure) were statistically significant to the inhibition efficiency values with *F*-values of 18.52 and −11.40 in solutions, and −11.01 and 7.83 in HCl solution. These values are greater than the significance factor (significance *F* in Tables 7 and 8) at $\alpha = 0.05$, thus they are significant at that level of probability. The statistical influence of the HMD concentration is 170.84% while the exposure time is −126.18% in H_2SO_4 depicting the overwhelming influence of HMD concentration on the values of inhibition efficiency from the experiments in comparison to the exposure time which is very negligible. In HCl only the exposure time (214.16%) is influential on the inhibition performance of HMD. The data from ANOVA tests are shown in Tables 7 and 8.

4. Conclusion

4-hydroxy-3-methoxybenzaldehyde (HMD) showed excellent corrosion inhibition at all concentrations studied due to the effective inhibiting action of the compound. The corrosion rates of the carbon steel samples were significantly reduced from the onset of exposure in HCl solution and at 216 h in H_2SO_4 solution. Molecular adsorption of HMD onto the steel surface was determined to obey the Langmuir adsorption isotherm model through chemisorption mechanism from thermodynamic calculations. Statistical derivations showed that inhibitor concentration only is relevant to the inhibition performance of HMD in H_2SO_4 and the exposure time only in HCl acid.

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References

Agarwal, P., & Landolt, D. (1998). Effect of anions on the efficiency of aromatic carboxylic acid corrosion inhibitors in near neutral media: Experimental investigation and theoretical modeling. *Corrosion Science, 40*, 673–691. http://dx.doi.org/10.1016/S0010-938X(97)00170-4

Ai, J. Z., Guo, X. P., Qu, J. E., Chen, Z. Y., & Zheng, J. S. (2006). Adsorption behavior and synergistic mechanism of a cationic inhibitor and KI on the galvanic electrode. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 281*, 147–155. http://dx.doi.org/10.1016/j.colsurfa.2006.02.031

Ajmal, M., Mideen, A. S., & Quraishi, M. A. (1994). 2-hydrazino-6-methyl-benzothiazole as an effective inhibitor for the corrosion of mild steel in acidic solutions. *Corrosion Science, 36*, 79–84. http://dx.doi.org/10.1016/0010-938X(94)90110-4

Alcohol Nomenclature. (n.d.). Retrieved October 20, 2015, from www2.chemistry.msu.edu/faculty/reusch/virttxtjml/alcohol1.htm

Aldehyde Chemical Compound. (n.d.). Retrieved November 12, 2015, from http://www.britannica.com/science/aldehyde

Aprael, S. Y., Anees, A. K., & Rafal, K. W. (2013). New method of GPS orbit determination from GCPS network for the purpose of DOP calculations. *Alexandria Engineering Journal, 51*, 129–136.

Bethencourt, M., Botana, F. J., Calvino, J. J., & Marcos, M. (1998). Lanthanide compounds as environmentally-friendly corrosion inhibitors of aluminium alloys: A review. *Corrosion Science, 40*, 1803–1819. http://dx.doi.org/10.1016/S0010-938X(98)00077-8

Corrosion Inhibitors. (n.d.). *Autolab application note COR05*. Retrieved from http://www.ecochemie.nl/download/Applicationnotes/Autolab_Application_Note_COR05.pdf

El Achouri, M., Infante, M. R., Izquierdo, F., Kertit, S., Gouttaya, H. M, & Nciri, B. (2001). Synthesis of some cationic gemini surfactants and their inhibitive effect on iron corrosion in hydrochloric acid medium. *Corrosion Science, 43*, 19–35. http://dx.doi.org/10.1016/S0010-938X(00)00063-9

El-Etre, A. Y. (1998). Natural honey as corrosion inhibitor for metals and alloys. i. copper in neutral aqueous solution. *Corrosion Science, 40*, 1845–1850. http://dx.doi.org/10.1016/S0010-938X(98)00082-1

El-Etre, A. Y. (2001). Inhibition of acid corrosion of aluminum using vanillin. *Corrosion Science, 43*, 1031–1039.

El-Rehim, S. S. A., Ibrahim, M. A. M., & Khaled, K. F. (1999). 4-Aminoantipyrine as an inhibitor of mild steel corrosion in HCl solution. *Journal of Applied Electrochemistry, 29*, 593–599. http://dx.doi.org/10.1023/A:1003450818083

El-Sayed, A. (1997). Phenothiazine as inhibitor of the corrosion of cadmium in acidic solutions. *Journal of Applied Electrochemistry, 27*, 193–200. http://dx.doi.org/10.1023/A:1018456008267

Emregül, K. C., & Hayvalı, M. (2004). Studies on the effect of vanillin and protocatechualdehyde on the corrosion of steel in hydrochloric acid. *Materials Chemistry and Physics, 83*, 209–216. http://dx.doi.org/10.1016/j.matchemphys.2003.08.030

Felicia, R. S., Santhanalakshmi, S., Wilson, S. J., John, A. A., & Susai, R. (2004). Synergistic effect of succinic acid and Zn^{2+} in controlling corrosion of carbon steel. *Bulletin of Electrochemistry, 20*, 561–565.

Feng, Y., Siow, K. S., Teo, W. K., & Hsieh, A. K. (1999). The synergistic effects of propargyl alcohol and potassium iodide on the inhibition of mild steel in 0.5 M sulfuric acid solution. *Corrosion Science, 41*, 829–852. http://dx.doi.org/10.1016/S0010-938X(98)00144-9

Greenwood, N. N., & Earnshaw, A. (1997). *Chemistry of the elements* (2nd ed., pp. 653–657). Oxford: Butterworth-Heinemann.

Hackerman, N., Snavely, Jr., E., & Payne, Jr., J. S. (1966). Effects of anions on corrosion inhibition by organic compounds. *Journal of the Electrochemical Society, 113*, 677–681. http://dx.doi.org/10.1149/1.2424089

Hosseini, M. G., Mertens, S. F. L., & Arshadi, M. R. (2009). Synergism and antagonism in mild steel corrosion inhibition by sodium dodecylbenzenesulphonate and hexamethylenetetramine. *Corrosion Science, 45*, 1473–1489.

Inhibitor Efficiency. (n.d.). Retrieved from http://www.corrosion-doctors.org/Inhibitors/Efficiency.htm

James, R. F. (n.d.). *Introduction to ethers*. Retrieved December 16, 2015, from www.3rd1000.com/chem301/chem301w.htm

Martinez, S. (2002). Inhibitory mechanism of mimosa tannin using molecular modeling and substitutional adsorption isotherms. *Materials Chemistry Physics, 77*, 97–102.

Melchers, R. E., & Jeffrey, R. (2004). Influence of water velocity on marine immersion corrosion of mild steel. *Corrosion, 60*, 84–94. http://dx.doi.org/10.5006/1.3299235

Melchers, R. E., & Jeffrey, R. (2005). Early corrosion of mild steel in seawater. *Corrosion Science, 47*, 1678–1693. http://dx.doi.org/10.1016/j.corsci.2004.08.006

Mu, G. N., Li, X. H., Qu, Q., & Zhou, J. (2006). Molybdate and tungstate as corrosion inhibitors for cold rolling steel in hydrochloric acid solution. *Corrosion Science, 48*, 445–459. http://dx.doi.org/10.1016/j.corsci.2005.01.013

Negm, N. A., Tawfik, S. M., Badr, E. A., Abdou, M. I., Ferial, M., & Ghuiba, F. M. (2015). Evaluation of some nonionic surfactants derived from vanillin as corrosion inhibitors for carbon steel during drilling processes. *Journal of Surfactants and Detergents, 18*, 413–418. http://dx.doi.org/10.1007/s11743-015-1672-z

Obot, B., Obi-Egbedi, N. O., & Umoren, S. A. (2009). Experimental and theoretical investigation of clotrimazole as corrosion inhibitor for aluminium in hydrochloric acid and effect of iodide ion addition. *Der Pharm Chemica, 1*, 151–166.

Ochoa, N., Moran, F., & Pébère, N. (2004). The synergistic effect between phosphonocarboxylic acid salts and fatty amines for the corrosion protection of a carbon steel. *Journal of Applied Electrochemistry, 34*, 487–493. http://dx.doi.org/10.1023/B:JACH.0000021702.49827.11

Oguzie, E. E. (2004). Influence of halide ions on the inhibitive effect of Congo red dye on the corrosion of mild steel in sulphuric acid solution. *Materials Chemistry and Physics, 87*, 212–217. http://dx.doi.org/10.1016/j.matchemphys.2004.06.006

Oguzie, E. E., Unaegbu, C., Ogukwe, C. N., Okolue, B. N., & Onuchukwu, A. I. (2004). Inhibition of mild steel corrosion in sulphuric acid using indigo dye and synergistic halide additives. *Materials Chemistry and Physics, 84*, 363–368. http://dx.doi.org/10.1016/j.matchemphys.2003.11.027

Quraishi, M. A., & Sardar, R. (2001). Corrosion inhibition of mild steel in hydrochloric acid by some aromatic hydrazides. *Materials Chemistry and Physics, 71*, 309–313. http://dx.doi.org/10.1016/S0254-0584(01)00295-4

Rosliza, R., Nora'aini, A., & Wan Nik, W. B. (2010). Study on the effect of vanillin on the corrosion inhibition of aluminum alloy. *Journal of Applied Electrochemistry, 40*, 833-840.

Saha, G., Kurmaih, N., & Hakerman, N. (1955). Specific adsorption. *The Journal of Physical Chemistry, 59*, 695–707.

Şahin, M., Bilgiç, S., & Yılmaz, H. (2002). The inhibition effects of some cyclic nitrogen compounds on the corrosion of the steel in NaCl mediums. *Applied Surface Science, 195*(1-4), 1–7. http://dx.doi.org/10.1016/S0169-4332(01)00783-8

Shahidi, M., Mansouri, R., Bahrami, M. J., & Hosseini, S. M. A. (2015). Electrochemical and quantum chemical study of vanillin as a green corrosion inhibitor for AA6061 in NaCl solution. *Journal of Physical & Theoretical Chemistry, 11*, 227–238.

Shetty, S. D., Shetty, P., & Nayak, H. V. S. (2006). Inhibition of mild steel corrosion in acid media by n-(2-thiophenyl)-n/-phenyl thiourea. *Journal of the Chilean Chemical Society, 51*, 849–853.

Singh, A., Ebenso, E. E., & Quraishi, M. A. (2012). *Corrosion inhibition of carbon steel in HCl solution by some plant extracts. International Journal of Corrosion.* doi:10.1155/2012/897430

Unuabonah, E., Olu-Owolabi, B., Adebowale, K. O., & Ofomaja, A. E. (2007). Adsorption of lead and cadmium ions from aqueous solutions by tripolyphosphate-impregnated Kaolinite clay. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 292*, 202–211. http://dx.doi.org/10.1016/j.colsurfa.2006.06.024

Valle-Quitana, J. C., Dominguez-Patiño, G. F., & Gonzalez-Rodriguez, J. G. (2014). Corrosion Inhibition of Carbon Steel in 0.5 M H 2 SO 4 by Phtalocyanine blue. *ISRN Corrosion,* 1–8. doi:10.1155/2014/945645

Xianghong, L., & Guannan, M. (2005). Tween-40 as corrosion inhibitor for cold rolled steel in sulphuric acid: Weight loss study, electrochemical characterization, and AFM. *Applied Surface Science, 252*, 1254–1265.

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